

LOW TEMPERATURE CATALYTIC COMBUSTION OF CARBON BY ALKALI METAL SALT/PEROVSKITE TYPE OXIDE MIXTURE

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Key words : Catalytic combustion, Alkali salt, Perovskite type oxide

Introduction

Alkali metal salts have been reported the best catalysts for the carbon combustion.^{1,2)} However, their active species have been recognized to vaporize out from the combustion zone.³⁾ Some transition metal oxides have been reported active to catalyze the combustion and gasification of carbon.^{4,5)} However, their intimate contact with the carbon substrate should be assured for the catalysis. Enhancement of catalytic activity has been examined by increasing dispersions and controlling composition.^{6,7)} However, maintenance of contact with the separate carbon grains to increase the conversion has not been attempted.

In the present study, catalytic activity of alkali metal salts supported on γ - Al_2O_3 and perovskite type oxide for the combustion of active carbon was studied, to find a way to realize the repeated contact of alkali metal species with carbon through their sublimation and precipitation over the surface of the perovskite type oxide. Influence of anions of salts, mixing procedures of the catalyst, support and carbon as well as the reaction temperature, were examined. The elution of active species was also estimated to observe the combustion of carbon placed at the down-stream of the catalyst bed.

Experimental

Activated carbon (AC) (Nacalai tesque inc.; surface area 370 m^2/g) was used, after washing with hydrochloric acid aq. to remove ash and heat treated at 973K for 8h in nitrogen. Ultimate analysis showed that resulting AC carried small amount of mineral matter (0.01wt%), being free from any detectable hydrogen, oxygen, nitrogen or sulphur. Supported catalysts were prepared by the impregnation. A prescribed amount of potassium metal salts (K_2CO_3 , KCl, K_2SO_4) were dissolved in deionized water.

The AC, Al_2O_3 (Nikkei Kinzoku Co. ,Ltd.), perovskite type oxide used as carrier material was dispersed in the solution and then heated to dryness at 363K for 12h. The catalyst loading was adjusted to 1.3×10^{-3} atom alkali per total amount of carrier and reactant (AC) (g).

Perovskite type oxide was prepared from the mixture of component metal nitrates or acetates, through vigorous mixing in water, freeze-dry and calcined at 1123K for 5h. X-ray diffraction analyses showed perovskite type structure of mixed oxide. Examined composition of perovskite was $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.45}\text{Pt}_{0.05}\text{O}_3$ (LSCMP).

A continuous flow reactor apparatus was operated under atmospheric pressure. In order to prevent local accumulation of heat, an initial ratio of AC to catalyst was 0.1. The mixture of AC and catalyst was dispersed on a ceramic foam (Brigstone Co. Ltd.). A thermocouple was located at the end of catalyst bed. N_2 was flowed during the heating to the reaction temperatures and the oxidant gas (N_2 containing 4% O_2) was introduced for the combustion. The gaseous products were analyzed by IR-spectrometer (Simadzu Co. ,Ltd.). The amount of AC consumed was determined by the product gas analysis.

Results

Catalytic activity of supported potassium carbonate catalysts

Figure 1 shows AC combustion catalyzed by supported K_2CO_3 as function of time at 723K. The activity of supported K_2CO_3 catalysts used in this study increased in the order; $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3 < \text{K}_2\text{CO}_3/\text{Pt-}\gamma\text{-Al}_2\text{O}_3 < \text{K}_2\text{CO}_3/\text{AC} < \text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ blended with LSCMP $< \text{K}_2\text{CO}_3/\text{LSCMP}$. The activity of supported K_2CO_3 catalysts was significantly influenced by the supports;

particularly, K_2CO_3 supported on LSCMP catalyst showed the largest activity among the catalysts tested. Because the activity of LSCMP was not so high, K_2CO_3 supported LSCMP performed the catalysis of very rapid combustion within 500 sec, increasing the conversion upto 100%. $K_2CO_3/\gamma-Al_2O_3$ physically blended with LSCMP showed high activity than $K_2CO_3/\gamma-Al_2O_3$, giving c.a.100% conversion within 2000 sec. K_2CO_3 supported on AC, Pt- $\gamma-Al_2O_3$, and $\gamma-Al_2O_3$ showed rapid combustion at low conversion level, however the conversion was saturated at 60%.

Catalytic activity of supported potassium salts

Figure 2 summarizes the activity of potassium salts supported on $\gamma-Al_2O_3$ blended with or without LSCMP at 723K. First of all, $KCl/\gamma-Al_2O_3$ showed the largest activity among the salts supported on $\gamma-Al_2O_3$, obtaining nearly 100% combustion by 3000 sec. The $K_2SO_4/\gamma-Al_2O_3$ exhibited the lowest activity.

The effectiveness of the blended catalysts with LSCMP depended very much on the type of potassium salts. The blended catalysts of $K_2CO_3/\gamma-Al_2O_3$ with LSCMP exhibited the strongest synergistic effect to show the largest activity among the potassium salts tested. KCl blended with LSCMP exhibited lower activity than $KCl/\gamma-Al_2O_3$.

Analysis for disappearance of potassium on catalysts

In order to estimate potassium amount on carriers after the combustion reaction, the catalytic combustion was repeated three times, using the same catalyst. $K_2CO_3/\gamma-Al_2O_3$ and $K_2CO_3/LSCMP$ were mixed with carbon respectively, and then were heated to 873K under air flow (700 ml/min.). The potassium element remaining on these catalysts was extracted with HCl aq., and analyzed by capillary zone electrophoresis(SZE). Table 1 showed the diminution ratio of the potassium amount before and after reactions. $K_2CO_3/\gamma-Al_2O_3$ lost significant amount of K after the reaction, but less loss of potassium was detected on $K_2CO_3/LSCMP$.

And then to estimate outflow of potassium element from catalyst bed to down-stream, the combustion reactions were executed at 723K. AC was mixed with $K_2CO_3/LSCMP$ and $K_2CO_3/\gamma-Al_2O_3$ respectively in the same way as mentioned above. Then AC was placed at the down-stream of the catalyst bed.

The results are shown in Figure 3. The activities of $K_2CO_3/LSCMP$ and $K_2CO_3/\gamma-Al_2O_3$ are in it for references. The conversion(X) in this figure is defined as

$$X = (W_o - W - W_b) / (W_o - W_b)$$

where W_o is the initial amount of AC, which was mixed with catalyst, W is the combustion amount of AC at reaction time, W_b is the combustion amount of AC without catalyst at reaction time.

The combustion profiles over $K_2CO_3/LSCMP$ were similar regardless of the down flow carbon. In contrast, $K_2CO_3/\gamma-Al_2O_3$ increased the conversion of AC when the AC free from catalyst was placed at the down stream. Some catalysts may be transferred bed carrying the catalyst to the down stream.

Influence of reaction temperature

Figure 5 shows the catalytic activity of $K_2CO_3/\gamma-Al_2O_3$, $K_2CO_3/LSCMP$, and blended $K_2CO_3/\gamma-Al_2O_3$ with LSCMP at 623~723K.

$K_2CO_3/LSCMP$ exhibited the highest activity of these three catalysts at this temperature range. Although the activity of $K_2CO_3/\gamma-Al_2O_3$ blended with LSCMP was same to that of $K_2CO_3/\gamma-Al_2O_3$ at 423 K, the blended catalyst exhibited the higher activity at higher temperatures.

Discussion

Potassium salts have been reported to catalyze the combustion of the carbon through their reduction into metal to activate oxygen⁸). The alkali metal can sublime to be mobile over the carbon substrates, maintaining the intimate contact for the catalytic activity. On the other hand, sublimed metal may flow out from the carbon bed, no catalytic activity being maintained. Thus, the sublimation and precipitation of the metal should be

balanced in the carbon bed for the maintenance of the catalytic activity.

LSCMP appears a unique support to perform such sublimation and precipitation for catalytic activity. Another role of the support is to influence the decomposition of potassium salts into active species, LSCMP appears to have such a role. Questions why LSCMP performs such roles are not answered in this paper. Further research is attempted.

KCl/ γ -Al₂O₃ exhibited a unique activity to show stable activity, achieving nearly 100% conversion. Active species for KCl/ γ -Al₂O₃ is now studied.

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Table Potassium diminution ratio of K
before and after reaction by CZE

Catalyst	Diminution ratio
K ₂ CO ₃ / γ -Al ₂ O ₃	55.5%
K ₂ CO ₃ /LSCMP	8.0%

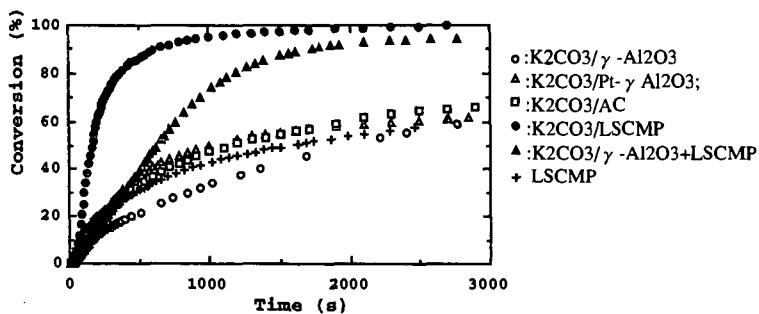


Fig.1 Conversion of carbon catalyzed by supported potassium carbonate

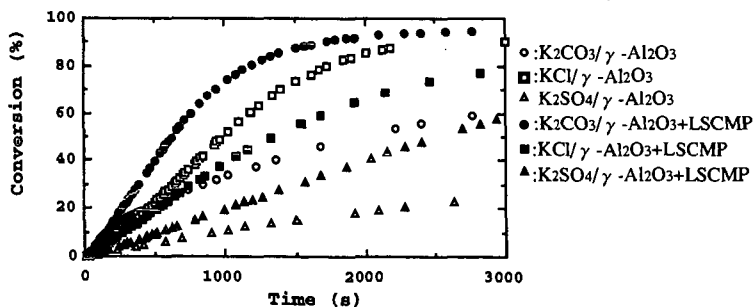


Fig.2 The activity of potassium salts supported on γ -Al₂O₃
blended with or without LSCMP

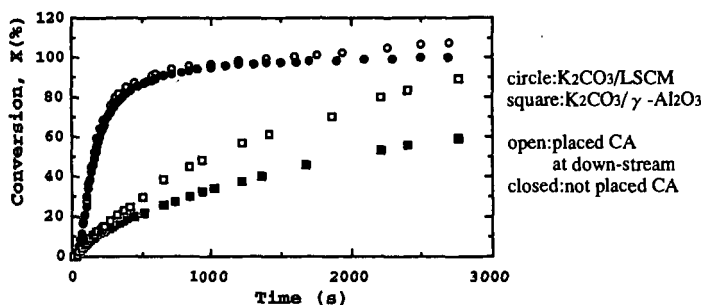


Fig.3 The combustion of carbon placed at down-stream of carbon/supported potassium carbonate bed

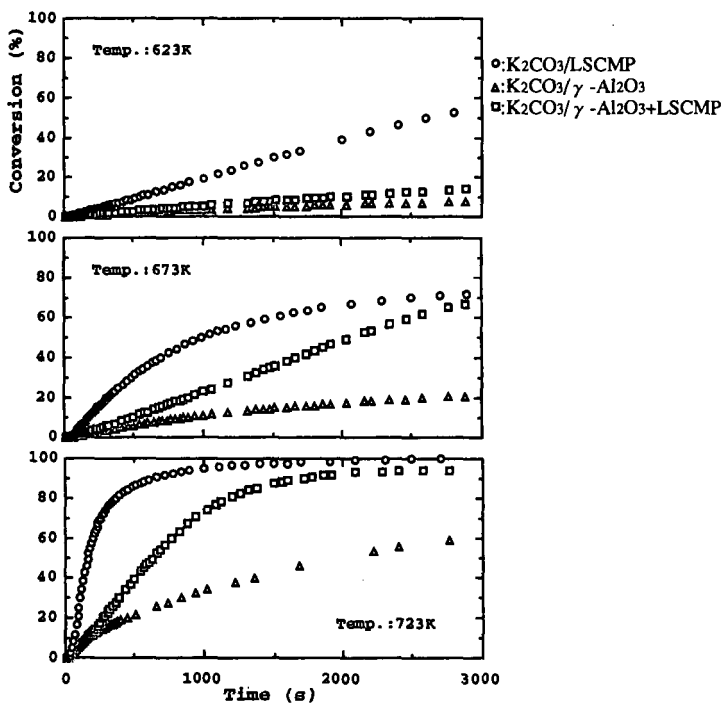


Fig.4 The activity of supported K_2CO_3 catalysts at some temperatures